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(54) Title: PROCESS FOR THE PRODUCTION OF MONOHALIDE OR DIHALIDE METALLOCENE COMPOUNDS

(57) Abstract: A process for preparing dihalide or monohalide metallocene compounds comprising contacting a compound of formula (II) $(Cp)(ZR^1_m)_n(A)_rML^y$, (II) wherein Cp is a cyclopentadienyl radical; $(ZR^1_m)_n$ is a divalent bridging group between Cp and A; A is a cyclopentadienyl radical or O, S, NR^2 , PR^2 wherein R^2 is an hydrocarbon radical, M is zirconium, titanium or hafnium, L' is an hydrocarbon radical, r ranges from 0 to 2 and y is equal to 4; with an halogenating agent selected from the group consisting of: $T^1L_{w^1}$ wherein T^1 is a metal of groups 3-13 of the periodic table; L is halogen and w^1 is equal to the oxidation state of the metal T^1 ; $T^2L_{w^2}$ wherein T^2 is a nonmetal element of groups 13-16 of the periodic table (new IUPAC version); and w^2 is equal to the oxidation state of the element T^2 ; $O=T^3L_{w^3}$ where T^3 is a selected from the group consisting of C, P and S; O is an oxygen atom bonded to T^3 through a double bond; and w^3 is equal to the oxidation state of the element T^3 minus 2; $R^6C(O)L$, wherein R^6 is an hydrocarbon radical; L_2 and HL.

PROCESS FOR THE PRODUCTION OF MONOHALIDE OR DIHALIDE METALLOCENE COMPOUNDS

The present invention relates to a process for the production of monohalide or dihalide metallocene compounds in high purity and in high yields.

Metallocene compounds are well known in the art as catalyst components for the polymerization of olefins. For instance, the European Patent Application EP 0 129 368 discloses catalysts comprising mono- and di-cyclopentadienyl coordination complexes with a transition metal in combination with an alumoxane.

In those metallocene compounds, the central metal is coordinated with one or more π -bonded ligands, usually cyclopentadienyl moieties, and with one or more sigma-bonded ligands. The latter are usually halogen, preferably chlorine. In the usual process for preparing dihalide metallocene compounds the lithium salts of the ligands are contacted with a tetrahalide of the metal. This process generates LiCl as a by-product that is difficult to separate because of the low solubility of the dihalide metallocene compounds in the usual solvents, and often the yield of the process is not satisfactory.

For instance, F. Wild et al. (*J. Organomet. Chem.*, 288:63-67, 1985) describe the synthesis of chiral ansa-zirconocene derivatives with ethylene-bridged ligands. In particular, it is reported the preparation of ethylene-bis(1-indenyl)zirconium dichloride by reaction of the dilithium salt of bis(1-indenyl)ethane with $ZrCl_4$, in a yield of about 35%. Better results have been obtained by I.M. Lee et al. (*Organometallics*, 11:2115-2122, 1992), who prepared ethylene-bis(1-indenyl)zirconium dichloride in a yield of 52%. Another example can be found in *Polyhedron* 1990, 9, 301 wherein it is reported the synthesis of bis(indenyl)zirconium dichloride starting from indene and zirconium tetrachloride with a final yield of 58%.

In *Izv. Akad. Nauk SSSR, Ser. Khim.* 1976, 2621 there is described a reaction of mercury chloride ($HgCl_2$) with bis(cyclopentadienyl)zirconium dibenzyl. In this paper it is shown that, instead of the expected bis(cyclopentadienyl)zirconium dichloride, the reaction product is the complex $(C_5H_5)_2ZrCl_2 \cdot 3C_6H_5CH_2HgCl$.

In *Dokl. Akad. Nauk SSSR* (1976), 231(1), 114-15, G. A. Razuvaev investigates the mechanism of photo or thermo demethylation and dearylation by using bis(cyclopentadienyl)zirconium dimethyl or dibenzyl and carbon tetrachloride or chloroform. The reaction is slow (about 100 h at 150°C for the thermodemethylation) and moreover the yields are rather low.

A process for obtaining bis(cyclopentadienyl)zirconium chloride methyl has been described by Wailes in Journal of Organometallic Chemistry 1972, 34, 155. According to this process, bis(cyclopentadienyl)zirconium chloride methyl is obtained by reacting the dimethyl derivative with PbCl_2 . The yield of this process is not reported. The applicant by running a test according to the process described by Wailes (reported as comparative example 11) has found that the yield of this process is not satisfactory for an industrial process.

Therefore it is felt the need for a simpler and more convenient and practical method to produce the above metallocene derivatives in satisfactory yields.

This need is fulfilled according to the present invention that, according to a first object, relates to a process for preparing dihalide or monohalide metallocene compounds of formula (I):



wherein $(\text{ZR}^1_m)_n$ is a divalent group bridging the Cp and A moieties; Z being C, Si, Ge, N or P, and the R^1 groups, equal to or different from each other, being hydrogen or linear or branched, saturated or unsaturated $\text{C}_1\text{-C}_{20}$ alkyl, $\text{C}_3\text{-C}_{20}$ cycloalkyl, $\text{C}_6\text{-C}_{20}$ aryl, $\text{C}_7\text{-C}_{20}$ alkylaryl or $\text{C}_7\text{-C}_{20}$ arylalkyl groups, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements, or two R^1 can form an aliphatic or aromatic $\text{C}_4\text{-C}_7$ ring that can bear substituents;

Cp is an unsubstituted or substituted cyclopentadienyl group, optionally condensed to one or more unsubstituted or substituted, saturated, unsaturated or aromatic rings, containing from 4 to 6 carbon atoms, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

A is O, S, NR^2 or PR^2 , R^2 being hydrogen, a linear or branched, saturated or unsaturated $\text{C}_1\text{-C}_{20}$ alkyl, $\text{C}_3\text{-C}_{20}$ cycloalkyl, $\text{C}_6\text{-C}_{20}$ aryl, $\text{C}_7\text{-C}_{20}$ alkylaryl or $\text{C}_7\text{-C}_{20}$ arylalkyl, or A has the same meaning of Cp;

M is zirconium, titanium or hafnium, preferably being zirconium or hafnium;

the L substituents, equal to or different from each other, preferably equal, are chlorine, bromine, iodine, preferably chlorine;

L' is selected from the group consisting of hydrogen, a linear or branched, saturated or unsaturated $\text{C}_1\text{-C}_{20}$ alkyl, $\text{C}_3\text{-C}_{20}$ cycloalkyl, $\text{C}_6\text{-C}_{20}$ aryl, $\text{C}_7\text{-C}_{20}$ alkylaryl or $\text{C}_7\text{-C}_{20}$ arylalkyl group, optionally containing one or more Si or Ge atoms; preferably L' is methyl, ethyl, n-butyl, sec-butyl, phenyl, benzyl or $-\text{CH}_2\text{Si}(\text{CH}_3)_3$; more preferably L' is methyl;

m is 1 or 2 depending on the oxidation state of Z, more specifically it is 1 when Z is N or P, and

it is 2 when Z is C, Si or Ge;

n is 0, 1, 2, 3 or 4, preferably it is 0, 1 or 2; being 0 when r is 0 or 2;

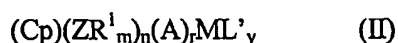
r is 0, 1 or 2, preferably being 0 or 1;

q is 1, 2, or 3;

s is 0 or 1;

s and q satisfying the following equation: $q+s=3-r$; preferably q is 1 or 2 and s is 0 or 1; more preferably q is 2 and s is 0;

said process comprising contacting a compound of formula (II):



wherein y is equal to $s+q$ and Cp, Z, R^1 , A, M, L' , m, r, n, s and q have the same meaning as above,

with an halogenating agent selected from the group consisting of T^1L_w^1 , T^2L_w^2 , $\text{O}=\text{T}^3\text{L}_w^3$, $\text{R}^6\text{C}(\text{O})\text{L}$, L_2 and HL, mercury dichloride (HgCl_2) being excluded, wherein:

T^1 is a metal of groups 3-13 of the periodic table (new IUPAC version) or of the lanthanides series; preferably T^1 is a metal of groups 7-11 of the periodic table (new IUPAC version);

T^2 is a nonmetal element of groups 13-16 of the periodic table (new IUPAC version) with the exclusion of carbon;

T^3 is selected from the group consisting of C, P and S;

O is an oxygen atom bonded to T^3 through a double bond;

R^6 is selected from a linear or branched, saturated or unsaturated C_1 - C_{20} alkyl, C_3 - C_{20} cycloalkyl, C_6 - C_{20} aryl, C_7 - C_{20} alkylaryl or C_7 - C_{20} arylalkyl;

L has the same meaning as above;

H is hydrogen;

w^1 is equal to the oxidation state of the metal T^1 ;

w^2 is equal to the oxidation state of the element T^2 ;

w^3 is equal to the oxidation state of the element T^3 minus 2.

The compound of formula (II) are well known in the art for example they can be easily prepared as described in WO 99/36427 or WO 00/75151.

An alternative embodiment for preparing dihalide or monohalide metallocene compounds of formula (I) starting directly from the ligand without isolating the compound of formula (II) comprises the following steps:

a) reacting a ligand of formula $(\text{Y-Cp})(\text{ZR}^1_m)_n(\text{A-Y})_r$ or when n is 0 a mixture of ligands Y-

Cp and $r(A-Y)$ with an amount EQ of a compound of formula L'_jB or $L'MgL'''$ such that $EQ \geq 1+r$ molar equivalents with respect to Cp, preferably $1+r \leq EQ \leq 1+r+q$ molar equivalents; more preferably $EQ = 1+r+q$ molar equivalents, wherein Cp, A, Z, R^1 , m, r, q, and L' have the meaning reported above; L''' is selected from the group consisting of chlorine, bromine, iodine; n is an integer having values 1, 2, 3 or 4; the groups Y, the same or different from each other, are suitable leaving groups; Mg is magnesium; B is an alkaline or alkaline-earth metal; and j is 1 or 2, j being equal to 1 when B is an alkali metal, and j being equal to 2 when B is an alkaline-earth metal;

- b) reacting the product obtained from step a) with at least 1 molar equivalent with respect to Cp of a compound of formula ML''_4 , wherein M have the meaning reported above, L'' is selected from the group consisting of chlorine, bromine, iodine;
- c) if the amount EQ of a compound of formula L'_jB or $L'MgL'''$ added in step a) is less than $1+r+q$, adding to the reaction mixture an amount of a compound of formula L'_jB or $L'MgL'''$ equal to or higher than $1+r+q-EQ$ molar equivalents, preferably equal to $1+r+q-EQ$;
- d) optionally purifying the mixture and separating the meso and the rac forms; and
- e) reacting the mixture with an halogenating agent selected from the group consisting of: $T^1L_w^1$; $T^2L_w^2$; $O=T^3L_w^3$; $R^6C(O)L$; L_2 and HL wherein T^1 , T^2 , T^3 , L, w^1 , w^2 , w^3 and R^6 have been described above.

When n is different from 0 and r is 1 a preferred process for preparing the dihalide or monohalide of bridged metallocene compounds of formula (III)



wherein M, Cp, A, Z, R^1 , m, q, s, L and L' have the meaning reported above and n is an integer having values 1, 2, 3 or 4; comprises the following steps:

- a) reacting a ligand of formula $(Y-Cp)(ZR^1_m)_n(A-Y)$ with at least $2+q$ molar equivalents with respect to Cp, of a compound of formula L'_jB or $L'MgL'''$, wherein Cp, A, Z, R^1 , m, q, and L' have the meaning reported above; L''' is selected from the group consisting of chlorine, bromine, iodine; n is an integer having values 1, 2, 3 or 4; the groups Y, the same or different from each other, are suitable leaving groups; Mg is magnesium; B is an alkaline or alkaline-earth metal; and j is 1 or 2, j being equal to 1 when B is an alkali metal, and j being equal to 2 when B is an alkaline-earth metal; and
- b) reacting the product obtained from step a) with at least 1 molar equivalent of a compound

of formula ML''_4 , wherein M have the meaning reported above, L'' is selected from the group consisting of chlorine, bromine, iodine;

- c) optionally purifying the mixture and separating the racemic and the meso forms;
- d) reacting the mixture with an halogenating agent selected from the group consisting of: $T^1L_w^1$; $T^2L_w^2$; $O=T^3L_w^3$; $R^6C(O)L$; L_2 and HL wherein T^1 , T^2 , T^3 , L , w^1 , w^2 , w^3 and R^6 have been described above.

When A is equal to Cp and n is equal to 0 a preferred process for preparing metallocene compounds of formula (IV)



wherein M, Cp, M, L, L' , r, q and s have been described above

comprises the following steps:

- a) reacting 1+r equivalent of a ligand of formula (Y-Cp) with at least 3+r molar equivalents of a compound of formula L_jB or $L'''MgL'$, wherein Cp, L''' and L' have the meaning reported above; the groups Y, the same or different from each other, are suitable leaving groups; B is an alkaline or alkaline-earth metal; and j is 1 or 2, j being equal to 1 when B is an alkali metal, and j being equal to 2 when B is an alkaline-earth metal;
- b) reacting the product obtained from step a) with at least 1 molar equivalent of a compound of formula ML''_4 , wherein M have the meaning reported above, L'' is selected from the group consisting of chlorine, bromine, iodine;
- c) optionally purifying the mixture; and
- d) reacting the mixture with an halogenating agent selected from the group consisting of: $T^1L_w^1$; $T^2L_w^2$; $O=T^3L_w^3$; $R^6C(O)L$; L_2 and HL wherein T^1 , T^2 , T^3 , L , w^1 , w^2 , w^3 , R^6 have been described above.

According to a preferred embodiment of the present invention, all the reactions of the above processes are carried out in an aprotic solvent, either polar or apolar. Said aprotic solvent is preferably an aromatic or aliphatic hydrocarbon, optionally halogenated, or an ether, more preferably it is selected from the group consisting of benzene, toluene, pentane, hexane, heptane, cyclohexane, dichloromethane, diethylether, tetrahydrofurane or mixtures thereof.

The amount of the halogenating agent to be used depends from the type of compound. As a rule, for obtaining a monohalide metallocene compounds at least half equivalent with respect to the halogen atom has to be used, while for obtaining a dihalide derivative at least one equivalent with respect to the halogen atom has to be used. Excess of halogenating agent can

also be used.

The Y leaving group is preferably hydrogen.

The ML''_4 reactant, is preferably selected from the group consisting of $TiCl_4$, $ZrCl_4$, $HfCl_4$. It can be used even in the form of a stabilized derivative, such as an etherate complex of ML''_4 , easily available on the market.

The compounds L'_jB and $L'''MgL'$ are alkylating agents. Preferably L' is selected from the group consisting of methyl, ethyl, n-butyl, sec-butyl, phenyl, benzyl and $-CH_2Si(CH_3)_3$. More preferably L' is methyl.

In the compound L'_jB , B is an alkali or alkaline-earth metal, preferably Li or Mg; j can be 1 or 2, as already reported.

The compound $L'''MgL'$ is a Grignard reagent, wherein Mg is magnesium and L''' and L' have the meanings reported above. L''' is preferably bromine or iodine.

According to a preferred embodiment of the process of the invention, said alkylating agent is methyllithium.

Preferably in the processes for preparing compounds of formula (I), (III) and (IV) in step (a), the ligands are previously dissolved in an aprotic polar solvent and to the resulting solution is added the alkylating agent L'_jB or $L'''MgL'$. This addition is preferably carried out at a temperature ranging from $-100^\circ C$ to $+80^\circ C$, more preferably from $-80^\circ C$ to $+10^\circ C$, over a period of 5 to 45 minutes, more preferably of 10 to 20 minutes. The alkylating agent is preferably added in the form of a solution in one of the above mentioned aprotic solvents, preferably dropwise.

The thus obtained reaction mixture is preferably allowed to react, under stirring, for a period ranging from 1 to 6 hours, more preferably from 2 to 3 hours, at a temperature comprised between $-10^\circ C$ and $+80^\circ C$, more preferably at room temperature.

Before the reaction with ML''_4 , in step (b), the mixture obtained from step (a) is preferably cooled to a temperature ranging from $-100^\circ C$ to $+80^\circ C$, more preferably from $-80^\circ C$ to $+70^\circ C$. Then ML''_4 is quickly added to the cooled slurry in the form of a solution in one of the above mentioned aprotic solvents, preferably pentane, hexane, heptane or toluene.

The reaction mixture is then allowed to react for a period ranging from 10 minutes to 36 hours, more preferably from 1 to 18 hours, at a temperature comprised between $-100^\circ C$ and $+80^\circ C$, more preferably between $-50^\circ C$ and $+50^\circ C$, even more preferably at room temperature.

In the halogenating step the temperature ranges from $-50^\circ C$ to $+150^\circ C$, preferably from $0^\circ C$ to $100^\circ C$, more preferably from $20^\circ C$ to $50^\circ C$. The halogenating agent is generally added

dropwise and then the reaction mixture is preferably allowed to react, under stirring, for a period ranging from 1 to 6 hours, more preferably from 2 to 3 hours, at a temperature comprised between -10°C and $+80^{\circ}\text{C}$, more preferably at room temperature.

The thus obtained metallocene compounds of formulas (I), (III) and (IV) can be isolated according to the common procedures known in the state of the art.

Non limiting examples of halogenating agents of formula T^1L_w^1 are: FeCl_3 , CuCl_2 and ZnCl_2 .

Non limiting examples of halogenating agents of formula T^2L_w^2 are: BCl_3 , BBr_3 , SiCl_4 and PCl_5 .

Non limiting examples of halogenating agents of formula $\text{O}=\text{T}^3\text{L}_w^3$ are: SOCl_2 and POCl_3 .

Non limiting examples of halogenating agents of formula $\text{R}^6\text{C}(\text{O})\text{L}$ are: $\text{CH}_3\text{C}(\text{O})\text{Cl}$, $\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{O})\text{Cl}$, $\text{C}_6\text{H}_5\text{C}(\text{O})\text{Cl}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{Cl}$.

Non limiting examples of halogenating agents of formula L_2 are: Br_2 , Cl_2 and I_2 .

Non limiting examples of halogenating agents of formula HL are HCl , HBr and HI .

In the optional steps (c) and (d) the purification of the reaction mixture is preferably carried out by simply filtering the solution in order to remove the salts. Also other systems of purification can be used, for example a suitable solvent in order to precipitate the undesired by products can be added with subsequently filtration. In these steps it is also possible to separate (when present) the racemic and the meso form by using methods known in the art. For example, by using suitable solvents it is possible to precipitate one form with subsequently filtration. All the operations are carried out in inert atmosphere.

In the metallocenes of formula (I) and (III), the divalent bridge $(\text{ZR}^1_m)_n$ is preferably selected from the group consisting of CR^1_2 , $(\text{CR}^1_2)_2$, $(\text{CR}^1_2)_3$, SiR^1_2 , GeR^1_2 , NR^1 and PR^1 , R^1 having the meaning reported above. More preferably, said divalent bridge is $\text{Si}(\text{CH}_3)_2$, SiPh_2 , CH_2 , $(\text{CH}_2)_2$, $(\text{CH}_2)_3$ or $\text{C}(\text{CH}_3)_2$.

The variable m is 1 or 2; the variable n ranges from 0 to 4 preferably is 1 or 2, when $n > 1$, the atoms Z can be the same or different from each other, such as in divalent bridges $-\text{CH}_2-\text{O}-$, $-\text{CH}_2-\text{S}-$ and $-\text{CH}_2-\text{Si}(\text{CH}_3)_2-$. When $n = 0$ and $r = 1$, A can have only the meaning of Cp .

In the metallocenes of formula (I), (III) and (IV) the ligand Cp , which is π -bonded to said metal M , is preferably selected from the group consisting of cyclopentadienyl, mono-, di-, tri- and tetra-methyl cyclopentadienyl; 4-tertbutyl-cyclopentadienyl; 4-adamantyl-cyclopentadienyl; indenyl; mono-, di-, tri- and tetra-methyl indenyl; 4,5,6,7-tetrahydroindenyl; fluorenyl; 5,10-dihydroindeno[1,2-b]indol-10-yl; N-methyl- or N-phenyl-5,10-dihydroindeno [1,2-b]indol-10-yl;

5,6-dihydroindeno[2,1-b]indol-6-yl; N-methyl-or N-phenyl-5,6-dihydroindeno[2,1-b]indol-6-yl; azapentalene-4-yl; thiapentalene-4-yl; azapentalene-6-yl; thiapentalene-6-yl; mono-, di- and tri-methyl-azapentalene-4-yl and 2,5-dimethyl-cyclopenta[1,2-b:4,3-b']-dithiophene.

The group A has preferably the same meaning of Cp, or it is N- methyl, N-ethyl, N-isopropyl, N-butyl, N-phenyl, N-benzyl, N-cyclohexyl and N-cyclododecyl.

Non limiting examples of metallocene compounds of formula (I) , (III) and (IV) are the racemic and the meso form (when present) of the following compounds:

bis(cyclopentadienyl)zirconium dichloride;

bis(indenyl)zirconium dichloride;

bis(tetrahydroindenyl)zirconium dichloride;

bis(fluorenyl)zirconium dichloride;

dimethylsilanediylbis(indenyl)zirconium dichloride,

dimethylsilanediylbis(2-methyl-4-phenylindenyl)zirconium dichloride,

dimethylsilanediylbis(4-naphthylindenyl)zirconium dichloride,

dimethylsilanediylbis(2-methylindenyl)zirconium dichloride,

dimethylsilanediylbis(2-methyl-(4-t-butyl-phenyl) indenyl)zirconium dichloride,

dimethylsilanediylbis(2-methyl-4-isopropylindenyl)zirconium dichloride,

dimethylsilanediylbis(2,4-dimethylindenyl)zirconium dichloride,

dimethylsilanediylbis(2-methyl-4,5-benzindenyl)zirconium dichloride,

dimethylsilanediylbis(2,4,7-trimethylindenyl)zirconium dichloride,

dimethylsilanediylbis(2,4,6-trimethylindenyl)zirconium dichloride,

dimethylsilanediylbis(2,5,6-trimethylindenyl)zirconium dichloride,

methyl(phenyl)silanediylbis(2-methyl-4,6-diisopropylindenyl)-
zirconium dichloride,

methyl(phenyl)silanediylbis(2-methyl-4-isopropylindenyl)-
zirconium dichloride,

1,3-propylenebis(indenyl)zirconium dichloride,

1,3-propylenebis(4,7-dimethylindenyl)zirconium dichloride,

1,3-propylenebis(2-methyl-4-phenylindenyl)zirconium dichloride,

1,3-propylenebis(2-methyl-4,6-diisopropylindenyl)zirconium dichloride,

1,3-propylenebis (2-methyl-4,5-benzindenyl)zirconium dichloride,

1,2-ethylenebis(indenyl)zirconium dichloride,

1,2-ethylenebis(4,7-dimethylindenyl)zirconium dichloride,
 1,2-ethylenebis(2-methyl-4-phenylindenyl)zirconium dichloride,
 1,4-butanediylbis(2-methyl-4-phenylindenyl)zirconium dichloride,
 1,2-ethylenebis(2-methyl-4,6-diisopropylindenyl)zirconium dichloride,
 1,4-butanediylbis(2-methyl-4-isopropylindenyl)zirconium dichloride,
 1,4-butanediylbis(2-methyl-4,5-benzoindenyl)zirconium dichloride,
 1,2-ethylenebis(2-methyl-4,5-benzoindenyl)zirconium dichloride,
 [4-(η^5 -cyclopentadienyl)-4,6,6-trimethyl(η^5 -4,5-tetrahydro-
 pentalene)]dichloridezirconium,
 [4-(η^5 -3'-trimethylsilylcyclopentadienyl)-4,6,6-trimethyl(η^5 -4,5-
 tetrahydropentalene)]dichloridezirconium,
 (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethane-
 dichloridetitanium,
 (methylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethylsilyl-
 dichloridetitanium,
 (methylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediyl-
 dichloridetitanium,
 (tertbutylamido)-(2,4-dimethyl-2,4-pentadien-1-yl)dimethylsilyl-
 dichloridetitanium,
 bis(1,3-dimethylcyclopentadienyl)zirconium dichloride,
 methylene(3-methyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'])
 dithiophene)zirconium dichloride;
 methylene(3-isopropyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'])
 dithiophene)zirconium dichloride;
 methylene(2,4-dimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'])
 dithiophene)zirconium dichloride;
 methylene(2,3,5-trimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'])
 dithiophene)zirconium dichloride;
 methylene-1-(indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'])dithiophene)zirconium
 dichloride;
 methylene-1-(indenyl)-7-(2,5-ditrimethylsilylcyclopentadienyl-[1,2-b:4,3-
 b'])dithiophene)zirconium dichloride;

methylene-1-(3-isopropyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dithiophene)zirconium dichloride;
methylene-1-(2-methyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dithiophene)zirconium dichloride;
methylene-1-(tetrahydroindenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dithiophene)zirconium dichloride;
methylene(2,4-dimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dioxazol)zirconium dichloride;
methylene(2,3,5-trimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dioxazol)zirconium dichloride;
methylene-1-(indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dioxazol)zirconium dichloride;
isopropylidene(3-methyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dithiophene)zirconium dichloride;
isopropylidene(2,4-dimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dithiophene)zirconium dichloride;
isopropylidene(2,4-diethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dithiophene)zirconium dichloride;
isopropylidene(2,3,5-trimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dithiophene)zirconium dichloride;
isopropylidene-1-(indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dithiophene)zirconium dichloride;
isopropylidene-1-(2-methyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dithiophene)zirconium dichloride;
dimethylsilandiyl-1-(2-methyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dithiophene)hafnium dichloride;
dimethylsilanediyl(3-tert-butyl-cyclopentadienyl)(9-fluorenyl)zirconium dichloride,
dimethylsilanediyl(3-isopropyl-cyclopentadienyl)(9-fluorenyl)zirconium dichloride,
dimethylsilanediyl(3-methyl-cyclopentadienyl)(9-fluorenyl)zirconium dichloride,
dimethylsilanediyl(3-ethyl-cyclopentadienyl)(9-fluorenyl)zirconium dichloride,
1-2-ethane(3-tert-butyl-cyclopentadienyl)(9-fluorenyl)zirconium dichloride,
1-2-ethane (3-isopropyl-cyclopentadienyl)(9-fluorenyl)zirconium dichloride,

1-2-ethane (3-methyl-cyclopentadienyl)(9-fluorenyl)zirconium dichloride,
1-2-ethane (3-ethyl-cyclopentadienyl)(9-fluorenyl)zirconium dichloride,
dimethylsilandiylbis-6-(3-methylcyclopentadienyl-[1,2-b]-thiophene) zirconium dichloride;
dimethylsilandiylbis-6-(4-methylcyclopentadienyl-[1,2-b]-thiophene)zirconium dichloride;
dimethylsilandiylbis-6-(4-isopropylcyclopentadienyl-[1,2-b]-thiophene)zirconium dichloride;
dimethylsilandiylbis-6-(4-ter-butylcyclopentadienyl-[1,2-b]-thiophene)zirconium dichloride;
dimethylsilandiylbis-6-(3-isopropylcyclopentadienyl-[1,2-b]-thiophene)zirconium dichloride;
dimethylsilandiylbis-6-(3-phenylcyclopentadienyl-[1,2-b]-thiophene)zirconium dichloride;
dimethylsilandiylbis-6-(2,5-dimethyl-3-phenylcyclopentadienyl-[1,2-b]-thiophene)zirconium
dichloride;
dimethylsilandiylbis-6-[2,5-dimethyl-3-(2-methylphenyl)cyclopentadienyl-[1,2-b]-
thiophene]zirconium dichloride;
dimethylsilandiylbis-6-[2,5-dimethyl-3-(2,4,6-trimethylphenyl)cyclopentadienyl-[1,2-b]-
thiophene]zirconium dichloride;
dimethylsilandiylbis-6-[2,5-dimethyl-3-mesitylenecyclopentadienyl-[1,2-b]-
thiophene]zirconium dichloride;
dimethylsilandiylbis-6-(2,4,5-trimethyl-3-phenylcyclopentadienyl-[1,2-b]-
thiophene)zirconium dichloride;
dimethylsilandiylbis-6-(2,5-diethyl-3-phenylcyclopentadienyl-[1,2-b]-thiophene)zirconium
dichloride;
dimethylsilandiylbis-6-(2,5-diisopropyl-3-phenylcyclopentadienyl-[1,2-b]-
thiophene)zirconium dichloride;
dimethylsilandiylbis-6-(2,5-diter-butyl-3-phenylcyclopentadienyl-[1,2-b]-
thiophene)zirconium dichloride;
dimethylsilandiylbis-6-(2,5-ditrimethylsilyl-3-phenylcyclopentadienyl-[1,2-b]-
thiophene)zirconium dichloride;
dimethylsilandiylbis-6-(3-methylcyclopentadienyl-[1,2-b]-silole)zirconium dichloride;
dimethylsilandiylbis-6-(3-isopropylcyclopentadienyl-[1,2-b]-silole)zirconium dichloride;
dimethylsilandiylbis-6-(3-phenylcyclopentadienyl-[1,2-b]-silole)zirconium dichloride;
dimethylsilandiylbis-6-(2,5-dimethyl-3-phenylcyclopentadienyl-[1,2-b]-silole)zirconium
dichloride;
dimethylsilandiylbis-6-[2,5-dimethyl-3-(2-methylphenyl)cyclopentadienyl-[1,2-b]-

silole]zirconium dichloride;
 dimethylsilandiylbis-6-[2,5-dimethyl-3-(2,4,6-trimethylphenyl)cyclopentadienyl-[1,2-b]-
 silole]zirconium dichloride;
 dimethylsilandiylbis-6-[2,5-dimethyl-3-mesitylenecyclopentadienyl-[1,2-b]-silole]zirconium
 dichloride;
 dimethylsilandiylbis-6-(2,4,5-trimethyl-3-phenylcyclopentadienyl-[1,2-b]-silole)zirconium
 dichloride;
 [dimethylsilyl(tert-butylamido)][(N-methyl-1,2-dihydrocyclopenta[2,1-b]indol-2-yl)]titanium
 dichloride;
 [dimethylsilyl(tert-butylamido)][(6-methyl-N-methyl-1,2-dihydrocyclopenta[2,1-b]indol-2-
 yl)]titanium dichloride;
 [dimethylsilyl(tert-butylamido)][(6-methoxy-N-methyl-1,2-dihydrocyclopenta[2,1-b]indol-2-
 yl)]titanium dichloride;
 [dimethylsilyl(tert-butylamido)][(N-ethyl-1,2-dihydrocyclopenta[2,1-b]indol-2-yl)]titanium
 dichloride;
 [dimethylsilyl(tert-butylamido)][(N-phenyl-1,2-dihydrocyclopenta[2,1-b]indol-2-yl)]titanium
 dichloride;
 [dimethylsilyl(tert-butylamido)][(6-methyl-N-phenyl-1,2-dihydrocyclopenta[2,1-b]indol-2-
 yl)]titanium dichloride;
 [dimethylsilyl(tert-butylamido)][(6-methoxy-N-phenyl-1,2-dihydrocyclopenta[2,1-b]indol-2-
 yl)]titanium dichloride;
 [dimethylsilyl(tert-butylamido)][(N-methyl-3,4-dimethyl-1,2-dihydrocyclopenta[2,1-b]indol-2-
 yl)]titanium dichloride;
 [dimethylsilyl(tert-butylamido)][(N-ethyl-3,4-dimethyl-1,2-dihydrocyclopenta[2,1-b]indol-2-
 yl)]titanium dichloride;
 [dimethylsilyl(tert-butylamido)][(N-phenyl-3,4-dimethyl-1,2-dihydrocyclopenta[2,1-b]indol-2-
 yl)]titanium dichloride;
 as well as the correspondent titanium and hafnium compounds and the dibromide and diiodide
 compounds.

The process according to the present inventions shows several advantages with respect to the
 processes generally known in the state of the art. The overall yields starting from the ligands

are generally higher than those reported in the art. Moreover, it is easier to purify the desired product, due to the better solubility of the formed intermediate alkylated metallocene with respect to the dihalide or monohalide product. Further, because of the higher solubility of said intermediate metallocene it is also easy to separate the racemic and the meso form at this step and thus to obtain the substantially pure racemic or meso form as the final product.

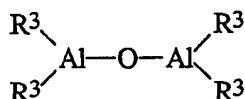
The metallocene compounds obtained with the process according to the present invention, in combination with a suitable activator such as an alumoxane, can be used as a catalyst for the polymerization of olefins. Particularly, they can be used for the homo or co-polymerization of alpha-olefins of formula $\text{CH}_2=\text{CHR}$ wherein R is hydrogen or a $\text{C}_1\text{-C}_{20}$ alkyl, such as propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene and 1-octene.

An interesting use is for the production of isotactic, syndiotactic or atactic polypropylene.

Another interesting use is for the copolymerization of ethylene with alpha-olefins, such as propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene and 1-octene, with cycloolefins, such as cyclopentene, cyclohexene, norbornene and 4,6-dimethyl-1-heptene, or with polyenes, such as 1,4-hexadiene, isoprene, 1,3-butadiene, 1,5-hexadiene and 1,6-heptadiene.

Further, they can be advantageously used in olefin oligomerization or hydrogenation reactions.

The above metallocenes form suitable polymerization catalytic systems in association with alumoxanes of formula:



wherein the substituents R^3 can be a linear or branched, saturated or unsaturated, $\text{C}_1\text{-C}_{20}$ alkyl, alkenyl or alkylaryl radical;

or in association with the product obtained by contacting an organometallic aluminum compound of formula $\text{AlR}^5_{3-2}\text{H}_2$, wherein R^5 can be $\text{C}_1\text{-C}_{10}$ alkyl, alkenyl or alkylaryl radicals, optionally containing one or more Si or Ge atoms, with water.

Particularly suitable alumoxanes, acting as cocatalysts with the above metallocenes, are methylalumoxane (MAO), tris(2-methyl-propyl)alumoxane (TIBAO) and 2,4,4-trimethyl-pentylalumoxane (TIOAO).

Non-limiting examples of organometallic aluminum compounds that, upon contacting with water, produce suitable cocatalysts are trimethylaluminum (TMA), tris(2,4,4-trimethyl-pentyl)aluminum (TIOA), tris(2-methyl-propyl)aluminum (TIBA), tris(2,3,3-trimethyl-butyl)aluminum, tris(2,3-dimethyl-hexyl)aluminum, tris(2,3-dimethyl-butyl)aluminum,

tris(2,3-dimethyl-pentyl)aluminum, tris(2,3-dimethyl-heptyl)aluminum, tris(2-methyl-3-ethyl-pentyl)aluminum and tris(2-ethyl-3,3-dimethyl-butyl).

The above catalysts can suitably be used on inert supports, such as silica, alumina, styrene/divinylbenzene copolymers, polyethylene or polypropylene, particularly for use in the gas phase polymerizations.

The olefin polymerization processes can be carried out in liquid phase, optionally in the presence of an inert hydrocarbon solvent, either aromatic (e.g. toluene) or aliphatic (e.g. propane, hexane, heptane, isobutane, cyclohexane and 2,2,4-trimethylpentane). The polymerization temperature generally ranges from about 0°C to about 250°C, and preferably from 20 to 150°C.

The following examples are given for illustrative and not limitative purposes.

GENERAL PROCEDURES AND CHARACTERIZATIONS

All operations were performed under nitrogen by using conventional Schlenk-line techniques. Solvents were purified by degassing with N₂ and passing over activated (8 hours, N₂ purge, 300 °C) Al₂O₃, and stored under nitrogen. MeLi (Acros), TiCl₄ (Aldrich), ZrCl₄ (Aldrich), HfCl₄ (Roc-Ric, 99.99% Hf), FeCl₃ (Aldrich), BCl₃ (Aldrich), CuCl (Carlo Erba, RPE-ACS, 95%) and SiCl₄ (Aldrich) were used as received. Technical indene (Aldrich) was purified by passing over activated Al₂O₃; All compounds were analyzed on an AC 200 Bruker spectrometer, by ¹H NMR (200.13 MHz, CD₂Cl₂, referenced against the middle peak of residual CHDCl₂ at 5.35 ppm, or C₆D₆, referenced against the peak of residual C₆D₅H at 7.15 ppm) and ¹³C NMR (50.323 MHz, Broad Band Decoupling, C₆D₆, referenced to the central line of C₆D₆ at 128.00 ppm). All NMR solvents were dried over P₄O₁₀ or CaH₂ and distilled before use. GC-MS analyses were carried out on a HP 5890 - series 2 gas-chromatograph and a HP 5970 mass spectrometer.

Comparative example 1 synthesis of Ind₂ZrCl₂

40 mL of a 1.5 M solution of BuLi in Et₂O (60 mmol) were added dropwise to 7.0 mL of indene (60.0 mmol) in 20 mL of THF, cooled to -78 °C. At the end of the addition, the solution was allowed to warm to room temperature and stirred for 1 hour, to give an orange solution. 7 g of ZrCl₄ (30.0 mmol) were dissolved in 30 mL of THF at -78 °C in a 100 mL flask equipped with reflux condenser (exothermic reaction). The mixture was allowed to reach room temperature with stirring, then refluxed for 30 min, to give a clear, brown solution. To this solution was added the THF solution of indenyllithium at room temperature with stirring, then the resulting suspension was stirred for two hours. The color turned yellow. The solvents

were removed under reduced pressure, the residue slurried in Et₂O and transferred into an extractor, washed with Et₂O until colorless, then extracted with CH₂Cl₂, the extract dried and washed again with Et₂O and then pentane, finally dried to give 4.35 g of yellow, analytically pure Ind₂ZrCl₂. Isolated yield 36.9 %.

Comparative example 2 synthesis of Ind₂ZrCl₂

9.9 mL of a 1.6 M solution of MeLi in Et₂O (15.8 mmol) were added dropwise to 1.97 g of technical indene (93.3 % by GC, 15.8 mmol) in 30 mL of Et₂O, at the end of the addition the mixture was stirred for 40 min at room temp., then it was added at once to 1.84 g of ZrCl₄ (7.9 mmol) slurried in 30 mL of pentane, then the resulting suspension was stirred for two hours. The color turned yellow. The product in pentane/Et₂O was transferred into an extractor, filtrated, the filtrate was discarded, the residue dried and extracted at reflux with 80 mL of CH₂Cl₂ for 5 hours. The extract was dried to give 2.08 g of lemon yellow Ind₂ZrCl₂, containing 4 mol% of Ind₂ZrClMe (¹H NMR). Isolated yield 67 %.

Example 3 synthesis of Ind₂ZrCl₂

Synthesis of Ind₂ZrMe₂.

15.8 ml of a solution of MeLi 1.6 M in Et₂O (25.3 mmol) were added at room temperature to a solution of 1.5 g (12.6 mmoles) of indene (Aldrich, 97.9 % by G.C.) in 30 ml of Et₂O in about 5 minutes (exothermic reaction). The mixture was stirred for 30 min, to give an orange solution. 1.47 g of ZrCl₄ (6.33 mmol) were slurried in 30 ml pentane. The ZrCl₄ slurry in pentane was quickly added to the Li salt solution in Et₂O (exothermic reaction). The reaction mixture was stirred for 30 min, and the yellow-brown suspension was treated as described above, to give 1.92 g (86.5 % yield) of a light yellow solid, which was characterized by ¹H NMR as spectroscopically pure Ind₂ZrMe₂.

Anal. Calcd for C₂₀H₂₀Zr: C, 68.32; H, 5.73; Zr, 25.94. Found: C, 67.3; H, 5.75; Cl, <0.05.

¹H-NMR (C₆D₆, δ, ppm): -0.50 (s, Ti-CH₃, 6H), 5.37 (t, Cp-H(2), 2H, J = 3.24 Hz), 5.78 (d, Cp-H(1,3), 4H, J = 3.24 Hz), 6.90-6.95 (m, Ar, 4H), 7.16-7.22 (m, Ar, 4H).

Synthesis of Ind₂ZrCl₂.

0.33 g of Ind₂ZrMe₂ (0.94 mmol) were charged in a 10 mL Schlenk tube, and dissolved in 4 mL of CD₂Cl₂. 0.485 g of CuCl (Carlo Erba, 95 %, 4.65 mmol) were added, and the mixture stirred at room temperature for 6 hours, when ¹H NMR showed the reaction to be complete. 20 mL of CH₂Cl₂ were added and the mixture was filtered over a G4 frit. The yellow-green solution was brought to dryness to give 0.34 g of yellow-green powder (yield 93 %) whose ¹H

NMR is identical to that of a true sample of $\text{Ind}_2\text{ZrCl}_2$.

^1H NMR (CD_2Cl_2 , δ , ppm): 6.23 (d, H(1-3), 4H, $J = 3.32$ Hz), 6.55 (t, H(2), 2H, $J = 3.32$ Hz), 7.28-7.37 (m, Ar, 4H), 7.60-7.69 (m, Ar, 4H).

Example 4 synthesis of $\text{Ind}_2\text{ZrCl}_2$

2.5 g of indene (92 %wt by GC, 19.8 mmol) were dissolved in 30 mL of Et_2O in a 250 mL Schlenk tube. 24.8 mL of MeLi 1.6 M in Et_2O (39.7 mmol) were added with stirring at room temperature (exothermic reaction). After stirring for 40 min, a yellow-orange solution was obtained, to which was added a suspension of 2.3 g of ZrCl_4 (9.9 mmol) in 40 mL of pentane (exothermic reaction, the mixture turns dark brown). The mixture was stirred at room temperature for two hours, then concentrated under reduced pressure to give a black powder, which was slurried in 50 mL of CH_2Cl_2 , cooled to 0°C , and added of 9.9 mL of BCl_3 1M in heptane (9.9 mmol). During the addition, the mixture turns from dark grey to dark green. This was allowed to warm to room temperature and stirred for 30 min at room temperature (complete conversion to the dichloride observed by ^1H NMR at this time), then filtered and extracted with the same CH_2Cl_2 for 8 hours on a continuous extractor (the product precipitates in part as a yellow solid during extraction), the extract concentrated under reduced pressure to give a yellow powder, 3.74 g (96 % yield based on Zr) of spectroscopically pure $\text{Ind}_2\text{ZrCl}_2$.

Example 5 synthesis of $\text{Ind}_2\text{ZrCl}_2$

0.25 g of $\text{Ind}_2\text{ZrMe}_2$ (0.71 mmol) were dissolved in 10 mL of CH_2Cl_2 in a 25 mL Schlenk tube, and 0.71 mL of BCl_3 1M in heptane (0.71 mmol) were added, a yellow precipitate start forming, and the slurry was stirred at room temperature for 1 hour, when ^1H NMR showed the conversion to $\text{Ind}_2\text{ZrCl}_2$ to be quantitative. The yellow suspension was brought to dryness to give 0.27 g of yellow, powdery, analytically pure $\text{Ind}_2\text{ZrCl}_2$ (yield 97 %). Its ^1H NMR is identical to that of a true sample of $\text{Ind}_2\text{ZrCl}_2$.

Example 6 synthesis of $\text{Ind}_2\text{ZrCl}_2$

0.172 g of $\text{Ind}_2\text{ZrMe}_2$ (0.49 mmol) were slurried in 5 mL of hexanes in a 10 mL Schlenk tube, and 0.49 mL of BCl_3 1M in heptane (0.49 mmol) were added at room temperature, and the mixture stirred for 2 hours, to give a 45:55 mixture of $\text{Ind}_2\text{ZrCl}_2$ and $\text{Ind}_2\text{ZrClMe}$ (^1H NMR), additional 0.3 mL of BCl_3 1M in heptane (0.3 mmol) and stirred for additional 2 hours. At this point the reaction is complete and the product is analytically pure by ^1H NMR.

Example 7 synthesis of $\text{Ind}_2\text{ZrCl}_2$

300 mg of $\text{Ind}_2\text{ZrMe}_2$ (20790/21, 0.85 mmol) were dissolved in 20 mL of Et_2O in a 50 mL

Schlenk tube. 0.95 mL of a 2M solution of HCl in Et₂O (Aldrich, 1.71 mmol) were added at room temperature. Gas evolution (CH₄) is observed, together with instantaneous formation of a yellow precipitate. Removing the solvent under reduced pressure gives 320 mg of pure Ind₂ZrCl₂, yield 96 %.

Example 8 synthesis of Ind₂ZrMeCl

380 mg of Ind₂ZrMe₂ (20790/21, 1.08 mmol) were dissolved in 5 mL of CH₂Cl₂ in a 10 mL Schlenk tube. 175 mg of anhydrous FeCl₃ (Aldrich, 99.9%, 1.08 mmol) were added at room temperature (immediate darkening to black), and then the mixture is heated at 40 °C for 6 hours. After 3 hours ¹H NMR shows the presence of a 98:2 mixture of Ind₂ZrClMe and residual Ind₂ZrMe₂ (yield of Ind₂ZrMeCl 98%).

Example 9 synthesis of Ind₂ZrI₂

164 mg of Ind₂ZrMe₂ (0.46 mmol) were dissolved in 2 mL of CD₂Cl₂ in a 10 mL Schlenk tube. 120 mg of I₂ crystals (0.47 mmol) were added at room temperature. The solution was warmed to 40 °C. After 5 min stirring the I₂ is fully solubilized, to give a bright orange solution that was stirred for 6 hours at 40 °C. ¹H-NMR analysis shows the presence of residual Ind₂ZrMe₂, and the two reaction products Ind₂ZrIMe and Ind₂ZrI₂, in the ratio 6:67:27.

Additional 60 mg of I₂ were added, and the solution stirred at room temperature for 72 hours. ¹H-NMR analysis shows conversion to the target Ind₂ZrI₂.

Ind₂ZrIMe: ¹H-NMR (CD₂Cl₂, δ, ppm): -1.47 (s, 3 H, Zr-CH₃), 6.09 (t, 2H, Cp-H₂, J = 3.52 Hz), 6.39 (m, 2H, Cp-H(1,3)), 6.54 (m, 2H, Cp-H(3,1)), 7.23-7.28 (m, 2H, Ar), 7.64-7.69 (m, 2H, Ar).

Ind₂ZrI₂: ¹H-NMR (CD₂Cl₂, δ, ppm): 2.19 (CH₃I, cfr. CH₃I in CDCl₃ = 2.16 ppm); 6.42 (d, Cp-H(1,3), 4H, J = 3.33), 6.64 (t, Cp-H(2), 2H, J = 3.33), 7.30-7.40 (m, Ar, 4H), 7.66-7.75 (m, Ar, 4H).

Example 10 synthesis of Ind₂TiClMe

Synthesis Ind₂TiMe₂

31.0 mL of MeLi 1.6 M in Et₂O (49.6 mmol) were added with stirring at room temperature to a solution of 3 g of indene (94 % by G.C., 24.3 mmol) in 30 mL of diethyl ether over a period of about 10 minutes (exothermic reaction). The Schlenk tube was kept in a water bath to remove the heat of reaction. The reaction mixture was stirred for 30 minutes. After this time the solution turned from light yellow to orange. 1.34 mL of TiCl₄ (99 %, 12.2 mmol) were

dissolved in 30 mL of pentane, and this solution was quickly added to the Li salt solution (exothermic reaction). The reaction mixture was stirred for two hours at room temperature with final formation of a dark brown suspension. The solvents were then removed under reduced pressure. The brown solid obtained was extracted in a Soxhlet apparatus with 80 mL of pentane. The filtrate was evaporated to dryness under reduced pressure to give 2.62 g of a yellow-brown powder (70 % metal-based yield).

Anal. Calcd for $C_{20}H_{20}Ti$: C, 77.93; H, 6.54; Ti, 15.53. Found: C, 74.7; H, 6.35; Ti, 14.6; Cl, <0.05.

1H -NMR (C_6D_6 , δ , ppm): -0.50 (s, Ti-CH₃, 6H), 5.37 (t, Cp-H(2), 2H, $J = 3.24$ Hz), 5.78 (d, Cp-H(1,3), 4H, $J = 3.24$ Hz), 6.90-6.95 (m, Ar, 4H), 7.16-7.22 (m, Ar, 4H)

Synthesis $Ind_2TiClMe$

0.43 g of Ind_2TiMe_2 (20790/77, 1.4 mmol) were dissolved in 15 mL of toluene in a 50 mL Schlenk. 0.32 mL of $SiCl_4$ (99%, 2.79 mmol) were added at room temperature and the solution warmed up to 50 °C and stirred for 3 hours. 1H NMR reveals the formation of a 70:30 mixture of $Ind_2TiClMe$ and Ind_2TiMe_2 . To bring the reaction to completion, another 2 equivalents of $SiCl_4$ (0.32 mL) were added, and the red-orange solution stirred for 3 additional hours at 50 °C, then dried, to give a quantitative yield of $Ind_2TiClMe$ as a brick red powder.

1H -NMR (C_6D_6 , δ , ppm): -0.08 (s, Ti-CH₃, 3H), 5.52 (t, Cp-H(2), 2H, $J = 3.33$ Hz), 5.80 (ddd, Cp-H(1 or 3), 2H, $J = 0.88, 1.96, 3.33$ Hz), 5.86 (ddd, Cp-H(3 or 1), 2H, $J = 0.88, 1.96, 3.33$ Hz), 6.85-7.31 (m, Ar, 8H).

Comparative example 11 synthesis of $Ind_2ZrClMe$

A slurry of 2.53 g of $PbCl_2$ (Aldrich, MW = 278.106, 9.10 mmol) in 15 mL of toluene was added to a solution of Ind_2ZrMe_2 (1.25 g, MW = 351.594, 3.56 mmol) in 35 mL of toluene, in a 100 mL Schlenk flask. The dark orange suspension obtained was stirred 38 hours at room temperature and 10 hours at 40-45 °C, during which time formation of a black powder was observed. The suspension was then filtered on a G4 frit and the filtrate was evaporated to dryness under reduced pressure to give 1.1 g of a dark yellow powder, which was characterized by 1H NMR as a mixture of $Ind_2ZrMeCl$ and Ind_2ZrCl_2 in the ratio 90/10.

0.63 g of this mixture were treated with 30 mL of toluene and 1.2 g of $PbCl_2$ (4.31 mmol). The suspension obtained was stirred for 30 hours at room temperature and 12 hours at 40°C. 1H NMR analysis showed decomposition of the product to indene. The yield of the reaction

to give $\text{Ind}_2\text{ZrClMe}$ is 74%

Comparative example 12

0.67 g of CeCl_3 (Aldrich, MW = 246.48, 2.72 mmol) were added to a suspension of $\text{Ind}_2\text{ZrMe}_2$ (experiment 20826/5, 0.91 g, MW = 351.594, 2.59 mmol) in 30 mL of toluene, in a 100 mL Schlenk flask. The light brown suspension obtained was stirred 24 hours at room temperature, but no reaction was observed by ^1H NMR analysis. It was then treated with additional 0.64 g of CeCl_3 (2.6 mmol) and stirred 3 hours at room temperature and 4 hours at 40°C . No reaction was observed by ^1H NMR.

Example 13 synthesis of $\text{Ind}_2\text{ZrCl}_2$

A solution of SCl_2 (Riedel de Haen, 0.16 g, MW = 102.966, 1.55 mmol) in 10 mL of CH_2Cl_2 was added to a brown suspension of $\text{Ind}_2\text{ZrMe}_2$ (experiment 20826/7-9, 0.55 g, MW = 351.594, 1.56 mmol) in 10 mL of CH_2Cl_2 . During the addition exothermicity was observed and the reaction mixture turned clearer. After 3 hours stirring at room temperature the reaction mixture turned reddish and ^1H NMR analysis showed a mixture of $\text{Ind}_2\text{ZrCl}_2$ and $\text{Ind}_2\text{ZrMeCl}$ in the ratio 61/39. Additional 0.055 g of SCl_2 (0.53 mmol) were added to the reaction mixture. After 1 hour stirring the brown suspension obtained was evaporated to dryness under reduced pressure to give 0.61 g (100 % metal-based yield) of a clear brown powder, which ^1H NMR analysis showed to be $\text{Ind}_2\text{ZrCl}_2$ with some impurities.

Example 14 synthesis of Ind_2ZrI_2

Crystals of I_2 (0.70 g, MW = 253.809, 2.76 mmol) were added to a suspension of $\text{Ind}_2\text{ZrMe}_2$ (experiment 20826/7-9, 0.48 g, MW = 351.594, 1.36 mmol) in 20 mL of CH_2Cl_2 . The orange suspension turned to dark purple in few minutes. After 30 minutes stirring at room temperature, the suspension was evaporated to dryness under reduced pressure to give 0.83 g (100 % yield) of an orange powder, which was characterized by ^1H NMR as pure Ind_2ZrI_2 .

^1H -NMR (CD_2Cl_2 , δ , ppm): 6.42 (d, 4H, Cp-H(1,3), $J = 3.33$ Hz); 6.64 (t, 2H, Cp-H(2), $J = 3.33$ Hz); 7.30-7.40 (m, 4H, Ar); 7.66-7.75 (m, 4H, Ar).

Example 15 synthesis of $\text{Ind}_2\text{ZrBr}_2$

A solution of 0.52 g of Br_2 (Fluka, 3.69 mmol) in 7 mL of CH_2Cl_2 was added to a solution of 0.65 g of $\text{Ind}_2\text{ZrMe}_2$ (1.85 mmol) in 20 mL of CH_2Cl_2 . The reaction was exothermic. The brown suspension obtained was stirred at room temperature for 18 hours and then evaporated to dryness under reduced pressure to give a reddish powder. This powder showed the presence of some impurity, so it was treated with ether and filtered. The residue was still not clean

enough, so it was treated with toluene and filtered. The filtrate was evaporated to dryness under reduced pressure to give pure $\text{Ind}_2\text{ZrBr}_2$ which was characterized by ^1H NMR.

^1H NMR (CD_2Cl_2 , δ , ppm): 6.28 (d, 4H, Cp-*H*(1,3), $J = 3.42$ Hz); 6.57 (t, 2H, Cp-*H*(2), $J = 3.42$ Hz); 7.30-7.38 (m, 4H, Ar); 7.63-7.70 (m, 4H, Ar).

Example 16 synthesis of $\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(t\text{-BuN})\text{TiClMe}$

0.69 mL of SiCl_4 (5.98 mmol) previously diluted in 2 mL of CH_2Cl_2 were added dropwise at room temperature to a solution of 0.98 g of $\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(t\text{-BuN})\text{TiMe}_2$ (obtained according to WO 00/75151) in 5 mL of CH_2Cl_2 . After 6h, the monochloro complex was obtained in nearly 100% yield.

Example 17 synthesis of (N-ethyl-5,6-dihydroindeno[2,1-b]indol-6-yl)(*t*-BuN)TiCl₂

0.71g of CuCl (6.85 mmol) were added at room temperature to a solution of 0.6g (1.37 mmol) of dimethylsilyl(*tert*-butylamino)(N-ethyl-5,6-dihydroindeno[2,1-b]indol-6-yl)dimethyl titanium (obtained according to WO 01/53360) in 5 mL of CH_2Cl_2 . The mixture of reaction was monitored by ^1H -NMR after 1 h, 4 h and one night of stirring. The suspension was filtered and the filtrate was dried in vacuo obtaining a red-brown sticky solid (yield 100%). ^1H -NMR shows the formation of dimethylsilyl(*tert*-butylamino)(N-ethyl-5,6-dihydroindeno[2,1-b]indol-6-yl)dichloro titanium.

Example 18 synthesis of (N-ethyl-5,6-dihydroindeno[2,1-b]indol-6-yl)(*t*-BuN)TiCl₂

0.7 mL (0.7 mmol) of BCl_3 1.0 M in heptane were added at 0 °C to a solution of 0.306 g (0.7 mmol) of dimethylsilyl(*tert*-butylamino)(N-ethyl-5,6-dihydroindeno[2,1-b]indol-6-yl)dimethyl titanium (obtained according to WO 01/53360) in 8 mL of Et_2O , after 2 hours of stirring at room temperature the ^1H -NMR analysis shows the formation of the dichloro complex. The solvent was dried in vacuo and the crude was washed with 7 mL of toluene, the residue was dried under reduced pressure, obtaining a red brown solid, which resulted almost pure desired product by ^1H -NMR (yield 100%).

^1H -NMR (C_6D_6 , δ , ppm): 0.61 (s, 3H, Si- CH_3); 0.75 (s, 3H, Si- CH_3); 1.15 (t, 3H, CH_3 , $J = 7.24$ Hz); 1.28 (s, 9H, *t*-Bu); 3.81 (q, 2H, CH_2 , $J = 7.24$ Hz); 6.98-7.92 (m, 8H, Ar).

^1H -NMR (CDCl_3 , δ , ppm): 1.01 (s, 3H, Si- CH_3); 1.10 (s, 3H, Si- CH_3); 1.36 (s, 9H, *t*-Bu); 1.54 (t, 3H, CH_3 , $J = 7.24$ Hz); 4.38 (q, 2H, CH_2 , $J = 7.24$ Hz); 7.21-8.05 (m, 8H, Ar).

CLAIMS

1. A process for preparing dihalide or monohalide metallocene compounds of formula(I)



wherein $(\text{ZR}^1_m)_n$ is a divalent group bridging Cp and A; Z being C, Si, Ge, N or P, and the R^1 groups, equal to or different from each other, being hydrogen or linear or branched, saturated or unsaturated $\text{C}_1\text{-C}_{20}$ alkyl, $\text{C}_3\text{-C}_{20}$ cycloalkyl, $\text{C}_6\text{-C}_{20}$ aryl, $\text{C}_7\text{-C}_{20}$ alkylaryl or $\text{C}_7\text{-C}_{20}$ arylalkyl groups optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements or two R^1 can form a aliphatic or aromatic $\text{C}_4\text{-C}_7$ ring that can bear substituents;

Cp is a substituted or unsubstituted cyclopentadienyl group, optionally condensed to one or more substituted or unsubstituted, saturated, unsaturated or aromatic rings, containing from 4 to 6 carbon atoms, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

A is O, S, NR^2 , PR^2 wherein R^2 is hydrogen, a linear or branched, saturated or unsaturated $\text{C}_1\text{-C}_{20}$ alkyl, $\text{C}_3\text{-C}_{20}$ cycloalkyl, $\text{C}_6\text{-C}_{20}$ aryl, $\text{C}_7\text{-C}_{20}$ alkylaryl or $\text{C}_7\text{-C}_{20}$ arylalkyl, or A has the same meaning of Cp;

M is selected from zirconium, titanium or hafnium;

L, equal to or different from each other are selected from the group consisting of chlorine, bromine, iodine;

L' is selected from the group consisting of hydrogen a linear or branched, saturated or unsaturated $\text{C}_1\text{-C}_{20}$ alkyl, $\text{C}_3\text{-C}_{20}$ cycloalkyl, $\text{C}_6\text{-C}_{20}$ aryl, $\text{C}_7\text{-C}_{20}$ alkylaryl or $\text{C}_7\text{-C}_{20}$ arylalkyl group, optionally containing one or more Si or Ge atoms;

m is 1 or 2, more specifically it is 1 when Z is N or P, and it is 2 when Z is C, Si or Ge;

n is 0, 1, 2, 3 or 4, being 0 when r is 0 or 2;

r is 0, 1 or 2;

q is 1, 2, or 3;

s is 0 or 1;

s and q satisfying the following equation: $q+s=3-r$;

said process comprising contacting a compound of formula (II)



wherein

Cp, Z, R^1 , A, M, L', m, r and n have been described above and y is equal to $s+q$ wherein

s and q have been described above;

with an halogenating agent selected from the group consisting of $T^1L_w^1$, $T^2L_w^2$, $O=T^3L_w^3$, $R^6C(O)L$, L_2 and HL , mercury dichloride ($HgCl_2$) being excluded, wherein:

T^1 is a metal of groups 3-13 of the periodic table (new IUPAC version) or of the lanthanides series;

T^2 is a nonmetal element of groups 13-16 of the periodic table (new IUPAC version) with the exclusion of carbon;

T^3 is selected from the group consisting of C, P and S;

O is an oxygen atom bonded to T^3 through a double bond;

R^6 is selected from a linear or branched, saturated or unsaturated C_1 - C_{20} alkyl, C_3 - C_{20} cycloalkyl, C_6 - C_{20} aryl, C_7 - C_{20} alkylaryl or C_7 - C_{20} arylalkyl;

L has the same meaning as above;

H is hydrogen;

w^1 is equal to the oxidation state of the metal T^1 ;

w^2 is equal to the oxidation state of the element T^2 ;

w^3 is equal to the oxidation state of the element T^3 minus 2.

2. The process according to claim 1 wherein divalent bridge $(ZR^1_m)_n$ is selected from the group consisting of CR^1 , $(CR^1)_2$, $(CR^1)_3$, SiR^1 , GeR^1 , NR^1 and PR^1 , wherein R^1 has been described in claim 1;

the ligand Cp, which is π -bonded to said metal M, is selected from the group consisting of cyclopentadienyl, mono-, di-, tri- and tetra-methyl cyclopentadienyl; 4-tertbutyl-cyclopentadienyl; 4-adamantyl-cyclopentadienyl; indenyl; mono-, di-, tri- and tetra-methyl indenyl; 4,5,6,7-tetrahydroindenyl; fluorenyl; 5,10-dihydroindeno[1,2-b]indol-10-yl; N-methyl- or N-phenyl-5,10-dihydroindeno [1,2-b]indol-10-yl; 5,6-dihydroindeno[2,1-b]indol-6-yl; N-methyl-or N-phenyl-5,6-dihydroindeno[2,1-b]indol-6-yl; azapentalene-4-yl; thiapentalene-4-yl; azapentalene-6-yl; thiapentalene-6-yl; mono-, di- and tri-methyl-azapentalene-4-yl and 2,5-dimethyl-cyclopenta[1,2-b:4,3-b']-dithiophene;

The group A has the same meaning of Cp, or it is N- methyl, N-ethyl, N-isopropyl, N-butyl, N-phenyl, N-benzyl, N-cyclohexyl and N-cyclododecyl.

3. The process according to claim 2 wherein the divalent bridge $(ZR^1_m)_n$ is selected from the group consisting of $Si(CH_3)_2$, $SiPh_2$, CH_2 , $(CH_2)_2$, $(CH_2)_3$ or $C(CH_3)_2$.
4. The process according to anyone of claims 1-3 wherein the halogenating agent is

selected from the group consisting of FeCl_3 , CuCl_2 , ZnCl_2 , BCl_3 , BBr_3 , SiCl_4 , PCl_5 , SOCl_2 , POCl_3 , $\text{CH}_3\text{C}(\text{O})\text{Cl}$, $\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{O})\text{Cl}$, $\text{C}_6\text{H}_5\text{C}(\text{O})\text{Cl}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{Cl}$, Br_2 , Cl_2 , I_2 , HCl , HBr and HI .

5. A process for preparing dihalide or monohalide metallocene compounds of formula(I)



wherein M, Cp, A, Z, R^1 , r, m, n, q, s, L and L' have the meaning reported in anyone of claims 1-4 comprising the following steps:

- reacting a ligand of formula $(\text{Y-Cp})(\text{ZR}^1_m)_n(\text{A-Y})_r$ or when n is 0 a mixture of ligands Y-Cp and $r(\text{A-Y})$ with an amount EQ of a compound of formula $\text{L}'_j\text{B}$ or $\text{L}'\text{MgL}''$ such that $\text{EQ} \geq 1+r$ molar equivalents with respect to Cp, wherein Cp, A, Z, R^1 , m, r, q, and L' have the meaning reported above; L''' is selected from the group consisting of chlorine, bromine, iodine; n is an integer having values 1, 2, 3 or 4; the groups Y, the same or different from each other, are suitable leaving groups; Mg is magnesium; B is an alkaline or alkaline-earth metal; and j is 1 or 2, j being equal to 1 when B is an alkali metal, and j being equal to 2 when B is an alkaline-earth metal;
 - reacting the product obtained from step a) with at least 1 molar equivalent of a compound of formula ML''_4 , wherein M have the meaning reported above, L'' is selected from the group consisting of chlorine, bromine, iodine;
 - if the amount EQ of a compound of formula $\text{L}'_j\text{B}$ or $\text{L}'\text{MgL}''$ added in step a) is less than $1+r+q$, adding to the reaction mixture an amount of a compound of formula $\text{L}'_j\text{B}$ or $\text{L}'\text{MgL}''$ equal to or higher than $1+r+q-\text{EQ}$ molar equivalents;
 - optionally purifying the mixture and separating the racemic and the meso forms; and
 - reacting the mixture with an halogenating agent selected from the group consisting of: T^1L_w^1 ; T^2L_w^2 ; $\text{O}=\text{T}^3\text{L}_w^3$; $\text{R}^6\text{C}(\text{O})\text{L}$; L_2 and HL wherein T^1 , T^2 , T^3 , L, w^1 , w^2 , w^3 and R^6 have been described in anyone of claims 1-4.
- The process according to claim 5 wherein the amount EQ added in step a) is such that $1+r \leq \text{EQ} \leq 1+r+q$;
 - The process according to claim 5 wherein the amount EQ added in step a) is such that $\text{EQ} = 1+r+q$;
 - The process according to anyone of claims 5-7 for preparing dihalide or monohalide metallocene compounds of formula (III):



wherein M, Cp, A, Z, R¹, m, q, s, L and L' have the meaning reported in anyone of claims 1-7 and n is an integer having values 1, 2, 3 or 4; comprising the following steps:

- a) reacting a ligand of formula (Y-Cp)(ZR¹_m)_n(A-Y) with at least 2+q molar equivalents with respect to Cp of a compound of formula L'_jB or L'^{'''}MgL^{'''}, wherein Cp, A, Z, R¹, L' and m have been described above, L^{'''} is selected from the group consisting of chlorine, bromine, iodine; n is an integer having values 1, 2, 3 or 4; the groups Y, the same or different from each other, are suitable leaving groups; Mg is magnesium; B is an alkaline or alkaline-earth metal; and j is 1 or 2, j being equal to 1 when B is an alkali metal, and j being equal to 2 when B is an alkaline-earth metal;
 - b) reacting the product obtained from step a) with at least 1 molar equivalent of a compound of formula ML^{''}₄, wherein M have the meaning reported above, L^{''} is selected from the group consisting of chlorine, bromine, iodine;
 - c) optionally purifying the mixture and separating the racemic and the meso forms; and
 - d) reacting the mixture with an halogenating agent selected from the group consisting of: T¹L_w¹; T²L_w²; O=T³L_w³; R⁶C(O)L; L₂ and HL wherein T¹, T², T³, L, w¹, w², w³ and R⁶ have been described in anyone of claims 1-7.
9. The process according to anyone of claims 5-7 for preparing dihalide or monohalide metallocene compounds of formula (IV):



wherein M, Cp, M, L, L', r, q and s have been described in any of claims 1-7 comprising the following steps:

- a) reacting 1+r equivalent of a ligand of formula (Y-Cp) with at least 3+r molar equivalents of a compound of formula L_jB or L^{'''}MgL', wherein Cp, L^{'''} and L' have the meaning reported in anyone of claims 1-5; the groups Y, the same or different from each other, are suitable leaving groups; B is an alkaline or alkaline-earth metal; and j is 1 or 2, j being equal to 1 when B is an alkali metal, and j being equal to 2 when B is an alkaline-earth metal;
- b) reacting the product obtained from step a) with at least 1 molar equivalent of a compound of formula ML^{''}₄, wherein M have the meaning reported above, L^{''} is selected from the group consisting of chlorine, bromine;
- c) optionally purifying the mixture; and

- d) reacting the mixture with an halogenating agent selected from the group consisting of: $T^1L_w^1$; $T^2L_w^2$; $O=T^3L_w^3$; $R^6C(O)L$; L_2 and HL wherein T^1 , T^2 , T^3 , L , w^1 , w^2 , w^3 , R^6 have been described in anyone of claims 1-4.
10. The process according to anyone of claims 1-9 wherein the reactions are carried out in an aprotic polar or apolar solvent.
 11. The process according to anyone of claims 5-10 wherein the leaving group Y is hydrogen.
 12. The process according to anyone of claims 5-11 wherein L' is selected from the group consisting of methyl, ethyl, n-butyl, sec-butyl, phenyl, benzyl and $-CH_2Si(CH_3)_3$; the substituents and L''' is bromine or iodine.
 13. The process according to anyone of claims 5-11 wherein the reactant ML'''_4 is selected from the group consisting of $TiCl_4$, $ZrCl_4$, $HfCl_4$.